Collinear versus non-collinear magnetic order in Pd atomic clusters

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We present a thorough theoretical assessment of the stability of non-collinear spin arrangements in small palladium clusters. We generally find that ferromagnetic order is always preferred, but that antiferromagnetic and non-collinear configurations of different sorts exist and compete for the first excited isomers. We also show that the relative stability of all these states is rather insensitive to the choice of atomic configuration for the pseudopotential used and to the approximation taken for the exchange and correlation potential. This result stands in stark contrast with the situation found for the bulk phases of Palladium.

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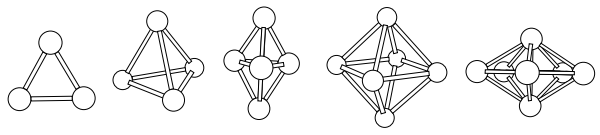
The magnetic properties of free-standing atomic clusters of 3d TM elements have been intensively scrutinized during the last two decades. Two different but related phenomena have specifically been discussed and essentially unravelled. The first is the modification of local magnetic moments as compared with the values found in bulk materials. The second is the competition between the possible ferromagnetic, antiferromagnetic and non-collinear arrangements of the local spins, as well as its interplay with the geometry of the nanostructure. In the case of ferromagnetic elements like Fe, Co and Ni, the increase of the average cluster magnetic moment can be easily explained in terms of the reduced atomic coordination in the low-dimensional regime, with oscillations associated to structural (symmetry) changes. [1] The case of antiferromagnets like Cr and Mn is much more complex. Atoms of these elements may display large magnetic moments, since they have a large number of d-holes susceptible to be polarized. On the other hand, clusters of these atoms may display tiny average magnetizations due to the tendency of their atomic moments to align in antiparallel directions. The structure plays also a fundamental role in the magnetic behavior of these clusters, since it may originate magnetic frustration. A conventional example of magnetic frustration in a classical spin system appears when atoms positions form triangular motifs. The studies of these classical systems show that magnetic frustration frequently leads to non-collinear configurations of the local spin moments. The latest theoretical studies reported in the literature show that non-collinear arrangements of quantum spins also appear as the ground or as some of the first isomers of clusters of $3d$ atoms, including not only Cr and Mn, but also Fe, Co and Ni.[2, 3, 4, 5, 6]

All materials made of $4d$ TM elements are paramagnets, in contrast to those of the $3d$ row. A natural question thus arises of whether small clusters of $4d$ elements may show low-lying magnetic states of collinear or even non-colinear nature. Bulk palladium, being a paramagnet in the brink of becoming a ferromagnet, presents one of the most intriguing and controversial magnetic behaviors in nature.[7] It is therefore not surprising that the very few experimental and theoretical studies published so far try to clarify whether Pd clusters of given sizes are magnetic or not, and what is the order of magnitude of their average magnetic moment. From the experimental side, most of the reports agree that only very small clusters have a net magnetic moment [8, 9, 10, 11], with the exception of Shinohara and coworkers, [12] who found noticeable magnetic moments at the surface of Pd particles as big as 79 Å. From the theoretical side, there is also consensus that very small Pd clusters are indeed magnetic.[13, 14, 15, 16, 17, 18] Futschek et al.[19] have studied recently small Pd clusters using Density Functional Theory (DFT) in the collinear framework, within a fixed-moment mode. They have found that multiple spin isomers exist for each cluster size with very small energy differences. Interestingly, some of these competing isomers present ferromagnetic order, while others display antiferromagnetic alignments, with possible frustration. Although Pd has tendency to ferromagentic order, this fact strongly points out to the possible existence of non-collinear magnetic structures, as a mechanism to release the frustration and competition between the different magnetic solutions.

We report in this article a thorough *Ab initio* study of the magnetic behavior of small palladium clusters Pd_N, with N ranging from 3 to 7. We have performed a simultaneous optimization of the geometric and magnetic degrees of freedom fully allowing for non-collinear spin arrangements. This consists, to the best of our knowledge, the first study of non-collinear magnetism in $4d$ atomic clusters. Moreover, a debate currently exists on the accuracy of the Local Density Approximation (LDA) [20] versus the Generalized Gradient Approximation (GGA) [21] for the determination of the magnetic behavior of low-dimensional Pd systems [16, 17, 18, 22, 23]. The present letter also assesses the reliability of both approximations for the case of free-standing Pd atomic clusters.

We have performed our calculations using the code



2.55 2.64 2.69 2.69 2.71

FIG. 1: Illustration of the ground state structures of the different clusters here studied and average interatomic distances (in Å) within GGA1.

TABLE I: Bindig energy of the ferromagnetic clusters in meV/atom.

N	LDA1	LDA3	GGA1	Ref.[18]	Ref.[19]
3	1.755	1.326	1.289	1.203	1.250
4	2.293	1.942	1.769	1.628	1.675
5	2.502	2.168	1.933	1.766	1.805
6	2.721	2.401	2.110	1.919	1.949
7	2.791	2.452	2.155	1.953	1.985

SIESTA.[24] SIESTA is a DFT method that employs linear combination of pseudoatomic orbitals as basis set. The electronic core is replaced by a nonlocal norm-conserving Troullier-Martins[25] pseudopotential that may include nonlinear core correction terms. The code allows to perform, together with the electronic calculation, structural optimization using a variety of algorithms. It also allows to simulate non-collinear spin arrangements both in the LDA and in the GGA approximations. [26]

In the present calculation, we have also used a variety of pseudopotentials to test their effect on free-standing clusters and their corresponding transferability. We have generated three different pseudopotentials using LDA. The first (LDA1) was built with the electronic configurations $5s^1$, $5p^0$ and $4d^9$, and core-corrections matching radius $r_c = 2.00$ a.u.; the second (LDA2) was identical to LDA1, but with $r_c = 1.2$ a.u.; the third had a closed-shell atomic configuration ($5s^0$, $5p^0$ and $4d^{10}$) and $r_c = 1.2$ a.u. We have also generated two GGA pseudopotentials with electronic configuration $5s^1$, $5p^0$ and $4d^9$, and $r_c = 2.0$ or 1.2 a.u. (GGA1 and GGA2, respectively). In all five cases, the cutoff radii of the s, p and d orbitals were taken at 2.30, 2.46 and 1.67 a.u., respectively. We have described valence states by a double-ζ polarized basis set (e.g.: two different radial functions for s and d orbitals and a single one for p orbitals). We have taken an energy cutoff of 150 Ry to define the real space grid for numerical integrations, but we checked that higher cutoffs did not alter the results. We have carried out the structural optimization using a conjugate gradient algorithm, where we have set the tolerance for the forces at 0.003 eV/Å, with eventual double-checks using 0.001 eV/Å.

We have found that the five pseudopotentials provide similar results when applied to an isolated palladium atom, being the eigenvalues of the ground state and different excited states slightly better reproduced with LDA1 and GGA1 (both had $r_c = 2.00$ a.u.). However, we have observed that they give rise to different magnetic behaviors when applied to the bulk fcc material. All LDA approximations give a lattice constant equal to 3.90 Å, while all GGA predict it to be equal to 4.01 Å. LDA1 gives a ferromagnetic ground state with $M \approx 0.54\mu_B$, while LDA2 and LDA3 predict the ground state to be paramagnetic. Finally, both GGA pseudopotentials lead to a ferromagnetic ground state with $M \approx 0.48\mu_B$. These results highlight the importance of testing all the different pseudopotentials for atomic clusters considered here.

Notice that we have not kept fixed the magnetic moment in our simulations of the Pd_N clusters, but rather have allowed it to vary freely during the non-collinear iterative selfconsistency process, in contrast to previous authors. Moreover, while we can not rule out that we may have missed low lying solutions, we have endeavored to minimize this risk by feeding a large variety of non-collinear seeds for each cluster. This effort has allowed us to find a rich and complex family of metastable solutions, that was absent in previous works. We finally note that we have repeated all calculations with the pseudopotentials LDA1, LDA3 and GGA1.

We have found that all clusters, except Pd_6, share the same collinear magnetic ground state, with a total spin of 2 μ_B, in agreement with previous authors [18, 19]. We should stress that all the tested pseudopotentials provide the same ground state, in stark contrast to the situation that arose for the bulk material. Moreover, we have found very similar inter-atomic distances for all Pd_N clusters, using whichever pseudopotential. These distances also agree with those obtained by Kumar and Futschek within a range of 1 per cent. The geometry of the ground state and the average interatomic distance of the Pd_N clusters is displayed in Fig. 1, where we show that these range from 2.55 Å in Pd_3 to 2.71 Å for Pd_7. We have written the binding energies of the different clusters in Table I. The table shows that GGA1 gives slightly smaller values than LDA1 and LDA3, as otherwise expected. Moreover, the binding energies predicted by GGA1 are very similar to those obtained by Kumar, who also used the GGA (within an ultrasoft pseudopotentials, plane waves code) and by Futschek et al., who used the all-electron VASP code, but did not state the approximation employed.

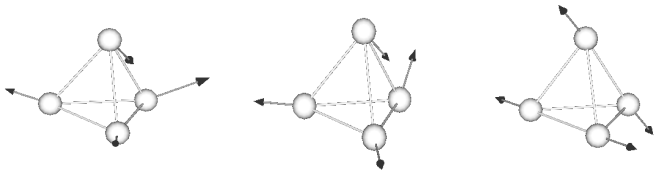


FIG. 2: Illustration of the non-colinear magnetic solutions for Pd_4 NC2 (LDA1), NC2 (LDA3) and NC1 (GGA1). The arrows are proportional to the size of the atomic moments.

TABLE II: Different solutions obtained for the Pd_N clusters. We provide the absolute values of the atomic magnetic moments, the total magnetic moment in the cluster $\bar{\mu}$ (both in units of μ_B) and the excitation energy per atom (in meV). For N=5 and 7, the first two values of the atomic moments correspond to the axial sites, whereas the last ones correspond to the planar sites.

	LDA1			LDA3			GGA1		
	Local moments	$\bar{\mu}$	ΔE	Local moments	$\bar{\mu}$	ΔE	Local moments	$\bar{\mu}$	ΔE
N=3									
Ferro.	(0.67×3)	**2**	0	(0.67×3)	**2**	0	(0.67×3)	**2**	0
AF							(0, 0.30, -0.30)	**0**	28
Radial							(0.18×3)	**0**	28
Para.	(0×3)	**0**	68	(0×3)	**0**	34	(0×3)	**0**	75
N=4									
Ferro.	(0.50×4)	**2**	0	(0.50×4)	**2**	0	(0.50×4)	**2**	0
NC1							(0.29,0.29,0.29,0.29)	**0**	12
NC2	(0.35,0.24,0.24,0.35)	**0.25**	9	(0.25,0.28,0.28,0.25)	**0.03**	10			
AF1	(0.32, 0.32, -0.32, -0.32)	**0**	26	(0,23, 0.23, -0.23, -0.23)	**0**	30	(0.29, 0.29, -0.29, -0.29)	**0**	25
AF2	(0.41, 0, -0.41, 0)	**0**	40	(0,31, 0, -0.31, 0)	**0**	31	(0.38, 0, -0.38, 0)	**0**	36
Para.	(0×4)	**0**	86	(0×4)	**0**	59	(0×4)	**0**	78
N=5									
Ferro.	(0.43,0.43,0.38×3)	**2**	0	(0.40×5)	**2**	0	(0.42,0.42,0.39×3)	**2**	0
AF1	(0, 0, 0.43, - 0.43, 0)	**0**	22	(0, 0, 0.33, - 0.33, 0)	**0**	19	(0, 0, 0.39, - 0.39, 0)	**0**	18
AF2	(0, 0, 0.48, -0.24, -0.24)	**0**	27				(0, 0, 0.44, -0.22, -0.22)	**0**	19
Radial	(0, 0, 0.29×3)	**0**	35				(0, 0, 0.27×3)	**0**	28
Para.	(0 ×5)	**0**	63	(0 ×5)	**0**	41	(0 ×5)	**0**	55
N=6									
Ferro.	(0.33×6)	**2**	0	(0.33×6)	**2**	0	(0.33×6)	**2**	0
Para.	(0×6)	**0**	- 13	(0×6)	**0**	- 12	(0×6)	**0**	- 4
N=7									
Ferro.	(0.19,0.19,0.32×5)	**2**	0	(0.21,0.21,0.31×5)	**2**	0	(0.20,0.20,0.32×5)	**2**	0
AF1	(-0.36,0.36,-0.33,-0.22,0.22,0.32,0)	**0**	9				(-0.32,0.32,-0.30,-0.20,0.20,0.30,0)	**0**	8
AF2	(0,0,-0.36,-0.23,0.23,0.36,0)	**0**	14	(0,0,-0.29,-0.20,0.20,0.29,0)	**0**	8	(0,0,-0.32,-0.21,0.21,0.32,0)	**0**	12
Radial	(0.27,0.27,0.18×5)	**0**	22	(0.24,0.24,0.12×5)	**0**	14	(0.24,0.24,0.17×5)	**0**	20
Para.	(0×7)	**0**	37	(0×7)	**0**	24	(0×7)	**0**	33

The Pd_6 cluster displays a behavior different from the rest, and therefore we discuss it separately. Futschek and coworkers [19] found that Pd_6 was also ferromagnetic in contrast to Kumar et al.[18], who predicted it to be paramagnetic. We have found that both states are nearly degenerate, with the paramagnetic solution being slightly more stable. Aditionally, we have been unable to find non-collinear or antiferromagnetic solutions for this cluster.

In contrast, and independently of the pseudopotential or approximation used, the rest of the clusters show a rich variety of antiferromagnetic and non-collinear solutions. Most of these solutions, though not all, exist for all LDA1, LDA3 and GGA1. We have also found that, whenever they exist, the relative order of the different solutions is maintained, and the size of the atomic moments is very similar. These facts strengthen our belief that Pd atomic clusters are much more insensitive to the pseudopotential and approximation employed than bulk Pd. It is also reassuring that most of the collinear solutions have been identified in previous calculations[19] (e.g.: AF1 for Pd_4 and Pd_5 and AF2 for Pd_7).

The non-collinear solutions found can be classified into those that release antiferromagnetic frustration and therefore have lower excitation energy than the AF solution (NC1 and NC2 in Pd_4, shown in Table II and Fig. 2), and radial or quasi-radial solutions, that resemble the hedgehogs found in low dimensional theories of classical or quantum antiferromagnets[27]. Hedgehogs in these theories do not release frustration but rather are excitations over the antiferromagnetic ground state. We also find that these radial states have a higher energy that the antiferromagnetic solution, and therefore do not release frustration.

Notice that the antiferromagnetic and non-collinear solutions can be reached at temperatures of the order of

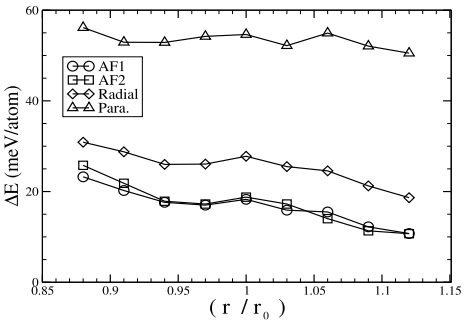


FIG. 3: Excitation energy per atom of the magnetic solutions of the Pd_5 cluster as a function of the average interatomic distance, using GGA1.

room temperatures (25 meV). Therefore, any measurement of the magnetization performed at room temperature should find a thermal average of all those states, many of which have a tiny magnetic moment. It should not be surprising that such a measurement give a small net moment.

We finally discuss the relationship between magnetism and equilibrium interatomic distances. We have found that these are essentially the same regardless of the magnetic state for the largest clusters (n = 5 - 7), the smallest ones showing slight variations of less than 0.04 Å, but only within the LDA solutions. We have additionally analyzed the relative stability of the different solutions as a function of the interatomic distance. To this aim, we plot the energy per atom of the low-lying excited states of the Pd_5 cluster, relative to the ground state energy, as a function of an uniform volume expansion, obtained using GGA1. The figure shows that no crossover takes place, apart from the nearly-degenerate AF1 and AF2 solutions, that cross at an expansion of about 4%. Moreover, the relative energy differences are essentially preserved and the local magnetic moments kept constant, except for the AF2 and radial solutions, where they slightly change (by about 10%).

To summarize, we have studied the geometry and magnetic properties of the ground state and lowest lying isomers of small palladium clusters Pd_N, with N ranging from 3 to seven. Our results confirm that the ground state is indeed collinear or paramagnetic. We have found a rich variety of non-collinear low-lying isomers, some of which efficiently release frustration, while other (hedgehog-like solutions) do not. All these solutions should contribute to the room temperature magnetic behavior of the clusters, probably rendering small measured magnetic moments. We have finally found that all these states are rather insensitive to the choice of the pseudopotential and to the approximation used for the exchange and correlation potential.

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